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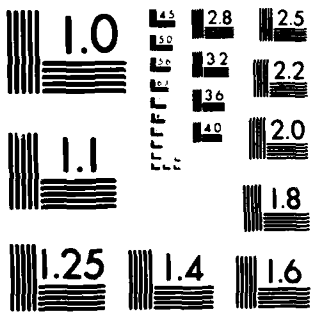

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The explosive RDX exhibits EPR signals when heated to temperatures ranging from 120°C to 200°C. Neat RDX samples give intense EPR signals at 197°C. RDX dissolved into sulfolane gives intense EPR signals at 170°C and weaker signals detected as low as 120°C. A 0.1M solution of RDX in sulfolane gives an EPR spectrum at 170°C which is attributed to a nitroxide radical [$H_2C(NNO_2)_2(CH_2)_2N$-O]. A 1M solution of RDX in sulfolane at 170°C and a neat sample of RDX at 197°C give an identical

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20. ABSTRACT (Continued)

spectrum of a second radical. This spectrum is simulated by the following combination of hyperfine couplings: (1) 1xI=1/2, A=9.98G; (2) 1xI=1, A=8.21G; (3) 4xI=1/2, A=6.66G; (4) 1xI=1/2, A=3.4G; (5) 1xI=1/2, A=1.25G.

CONTENTS

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EPR SPECTROSCOPY OF THERMALLY INITIATED FREE RADICALS IN RDX

INTRODUCTION

Free-radicals in RDX [$C_3H_6N_6O_6$; hexahydro-1,3,5-trinitro-5-triazine; cyclotrimethylene-trinitramine; cyclonite; hexogen] have been observed by both thermal and photochemical initiation.[1-5] Thermal initiation of solid-state explosives is accompanied by an increase in temperature (described as the "exotherm").[6] An exotherm is not unusual since many common reactions proceed through exothermic pathways. For example the oxidation of sugar by burning is exothermic. The unusual characteristic of explosives is the very rapid rate of <u>intense</u> heat evolution during thermal initiation.

We are investigating the production of free radicals in some common explosives by using EPR and NMR spectroscopy. The purpose of this article is to demonstrate the cw EPR detection of free radicals in the explosive RDX at temperatures below the "normal" decomposition temperature of neat RDX (205-206°C). This was accomplished by dissolving RDX into sulfolane [$C_4H_8O_2S$; Tetrahydrothiophene 1,1-dioxide] and heating the solution. EPR of neat RDX during heating was also recorded. Some of our previous work on RDX includes photochemically produced free radicals. This article reports free radicals produced strictly by thermal energy. Future studies are planned to look for transient free radicals (free radicals with millisecond lifetimes).

EXPERIMENTAL RESULTS

The EPR spectra were recorded with an IBM ER 200 x-band spectrometer. The modulation frequency was 100 KHz, the modulation amplitude was 0.63 G, and the microwave power was 8 milliwatts. Samples were heated in the cavity by flowing compressed air through a resistive heating coil. A Varian 4540 controller was used to regulate current to the heating coil. The temperature controller was calibrated with a chromel-alumel thermocouple. A quartz insert dewar was used to minimize heating of the cavity. Samples of neat RDX were heated in a standard 3mm i.d. quartz tube. Samples of RDX plus sulfolane were heated in a 1mm i.d. sample tube. (Sulfolane contributes to loss in cavity Q which necessitates small sample tubes.) The sample tubes were open to the air at 1 atm. No background EPR signals were observed from neat samples of sulfolane or DMSO (used as a solvent in some experiments) when heated to 200°C. The measurement of g-values was accomplished with an internal Mn^{2+} standard.

Some facts about sulfolane: At room temperature sulfolane is a solid, but above its melting point (m.p. 27.4-27.8°C) it becomes liquid and is miscible with water, acetone and toluene. RDX dissolves in sulfolane and forms a 1:1 complex at room temperature.[7] Above 70°C the complex dissociates into one RDX molecule and one sulfolane molecule, so at temperatures above 70°C complexing is not a problem. Five ml of sulfolane at 70°C dissolves greater than 100 mg of RDX without saturating. In the EPR experiments RDX was dissolved in sulfolane to form solutions ranging in

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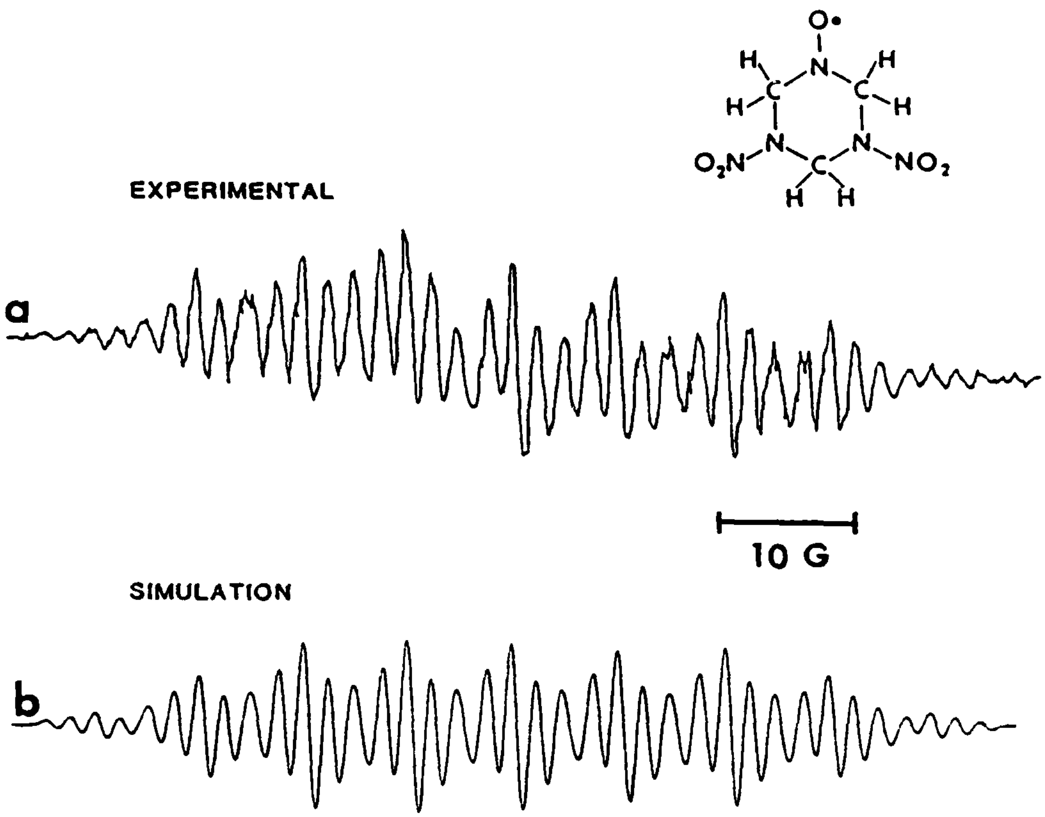
concentration from 0.1M to 1M. Because the boiling point of sulfolane (b.p. 285°C) is much greater that the decomposition temperature of RDX it is possible to decompose the RDX while it is still in solution. When the solutions were heated, spectra were observed at a temperature as low as 120°C. The optimum temperature where the EPR signals were strongest was 170°C. At 190°C outgassing of the sample tended to detune the microwave bridge.

In the first experiment an 0.1M solution of RDX in sulfolane was heated to 170°C and the spectrum shown in Fig. 1a was recorded. This EPR spectrum has 29 lines which are visible above the background noise. Using high gain weaker signals were observed at the field extrema of the spectrum. This spectrum is assigned to three inequivalent hyperfine couplings. The largest coupling is from a single ^{14}N (I=1) coupling of 15.8 G. The ^{14}N contributes 3 lines with an intensity ratio of 1:1:1. The second coupling is from four equivalent protons ($I={}^1/_2$) of 7.7 G. The intensity ratio of this quintet is 1:4:6:4:1. The third coupling is from two equivalent ^{14}N nuclei of 1.8 G. The intensity ratio of this quintet is 1:2:3:2:1. These couplings were used to compute a simulation of the spectrum which is shown in Fig. 1b. The EPR spectrum in Fig. 1a-b is attributed to a nitroxide free radical having the molecular structure I. This free radical is formed after net loss of NO from the RDX parent molecule. The same free radical has been observed by photo-chemical generation in an RDX- acetonitrile solution.[8] We have also observed similar radicals produced by photolysis of RDX-DMSO solutions.[3] After prolonged heating (about 1 hour) the spectrum in fig. 1a changed to a different spectrum (not shown) which is attributed to a different free radical.

In a second EPR experiment a 1M solution of RDX in sulfolane was heated to 170°C and the spectrum shown in Fig. 2a was recorded. This EPR spectrum has 36 lines. The 4 highest field lines and the 4 lowest field lines are obscured by the noise. The spectrum is symmetric, but there is no EPR line at center field. There is an apparent background signal which has a broad linewidth (approximately 25 Gauss). No attempt was made to analyze this background signal. Computer simulation of the spectrum in Fig. 2a was difficult but a reasonably accurate "fit" to the spectrum is shown in Fig. 2b. The simulation required 5 inequivalent couplings. The largest coupling is assigned to a nuclear spin $^1/_2$ coupling of 9.98 G and contributes a doublet with each line of equal intensity. The second coupling is assigned to a spin 1 coupling of 8.21 G which contributes a triplet of equal intensity. The third coupling of 6.66 G is assigned to 4 equivalent spin $^1/_2$ nuclei which contribute a quintet of lines with an intensity ratio of 1:4:6:4:1. The fourth coupling is assigned to a spin $^1/_2$ coupling of 3.4 G which contributes a doublet. The fifth coupling is assigned to another spin $^1/_2$ coupling of 1.25 G which contributes a doublet of lines. (These assignments are listed more conveniently in Fig. 2b.) As in Figure 1 there is a broadline signal with approximately 25 G linewidth which is included in the simulation shown in Fig. 2b. In many cases it is possible to rely upon computer simulations to unambiguously assign a radical structure. Such is not the case here because the parameters which are used to calculate the simulation are not unique. There are four different parameters which can be simultaneously varied: 1) the number of inequivalent couplings; 2) the nuclear spin number (I=1 or $^1/_2$); 3) the number of equivalent spins; and 4) the value of the hyperfine coupling. As the number of inequivalent couplings increases (in this case 5 inequivalent



I	EQUIVALENT SPINS	HYPERFINE COUPLINGS	INTENSITY RATIOS
1	1	15.8 GAUSS	1:1:1
1/2	4	7.7	1:4:6:4:1
1	2	1.8	1:2:3:2:1

Fig. 1. (a) This first derivative EPR spectrum was recorded with an 0.1M sample of RDX in sulfolane at 170°C. (b) The spectrum was computer simulated. The simulation required three ^{14}N couplings and a coupling from four equivalent protons.

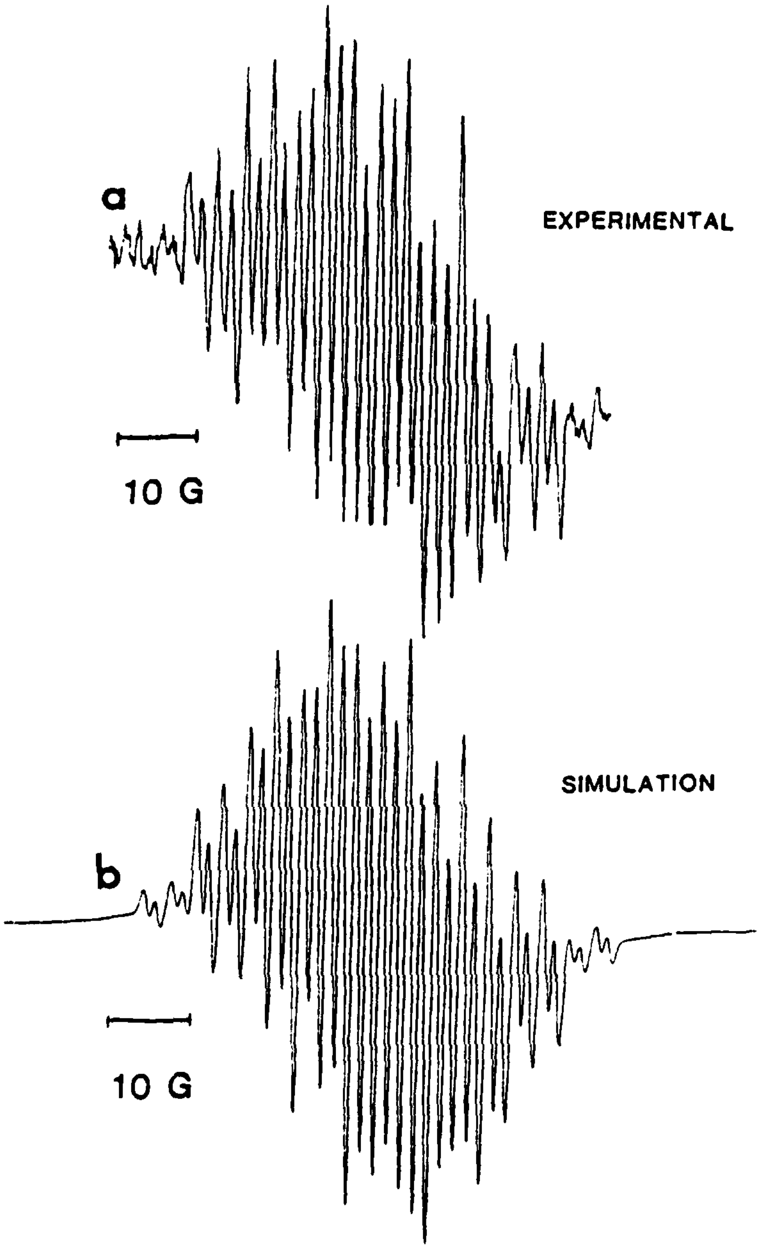


Fig. 2. (a) This first derivative EPR spectrum was recorded from a 1M sample of RDX in sulfolane at 170°C.

(b) The spectrum was computer simulated by using the following couplings:

1) $1xI={}^{1}/_{2}$ A=9.98 G
2) $1xI=1$ A=8.21 G
3) $4xI={}^{1}/_{2}$ A=6.66 G
4) $1xI={}^{1}/_{2}$ A=3.4 G
5) $1xI={}^{1}/_{2}$ A=1.25 G

couplings are used) the probability of a unique "fit" decreases because the total number of variables increases. For example substituting 2 equivalent spin 1 couplings for the 4 equivalent spin $^1/_2$ couplings in this assignment results in an almost identical spectrum (not shown; the total number of lines remains the same, but subtle differences in relative peak intensities occur). Further attempts to substitute different equivalent combinations of hyperfine couplings into Fig. 2b were not conclusive. From these results: 1) It is possible to simulate the experimentally observed spectrum (Fig. 2a) as a single radical (neglecting the broadline background signal). 2) The hyperfine couplings shown in Fig. 2b may be used in deducing a structure for the radical but a different set of equivalent couplings would lead to a different interpretation of the radical's structure.

In a third experiment 100 mg of neat RDX was heated to 197°C. The EPR spectrum which was recorded (Fig. 3) is identical to the spectrum in Fig. 2a-b. (The magnetic field sweep width is different in Fig. 2a and Fig. 3.) This indicates that the same free radical is detected in a 1M solution of RDX dissolved in sulfolane at 170°C and in neat RDX at 197°C. At 197°C the RDX is apparently molten and forms a solution phase environment containing the free radicals. Prolonged heating of the neat RDX at 197°C results in decomposition and gas evolution. Much of the sample eventually passes as a gas from the tube.

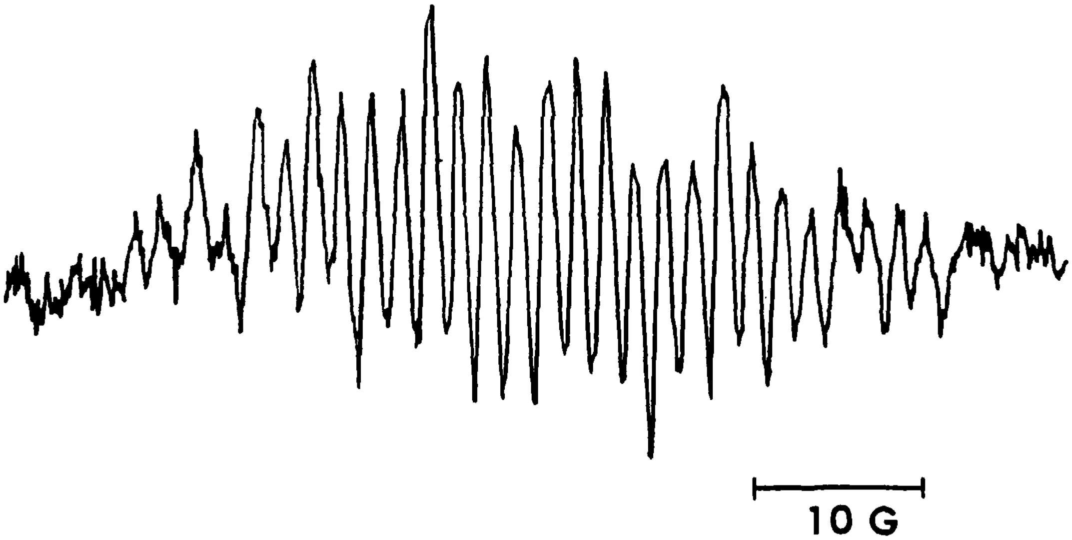


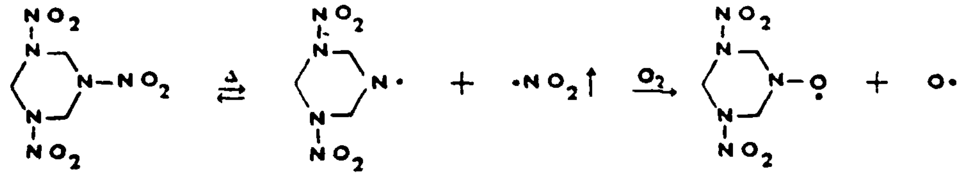
Fig. 3. *This first derivative EPR spectrum was recorded from 100 mg of* neat RDX at 197°C. The spectrum is the same as in Fig. 2a. (The magnetic field calibration between Fig. 2a and Fig. 3 is different and the signals in Fig. 3 are weaker that those in Fig. 2a. The background signal in Fig. 3 is not as intense as in Fig. 2a.)

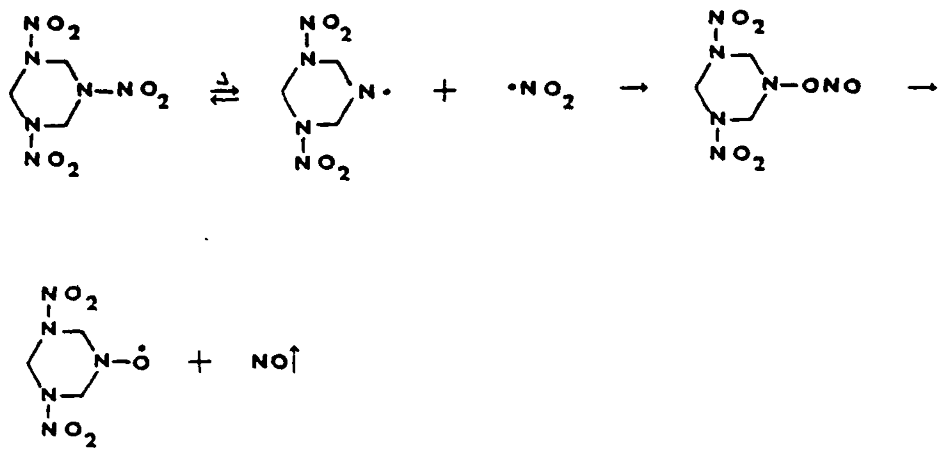
DISCUSSION

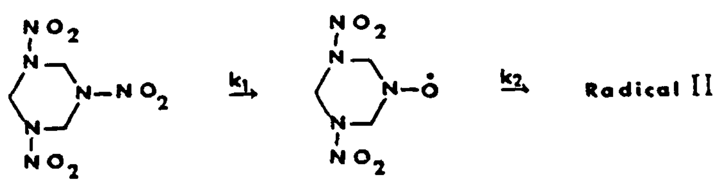
Many different pathways for the thermal decomposition of RDX have been suggested. Two categories for describing initial decomposition steps include: 1) decomposition with the molecular ring intact and 2) decomposition involving cleavage of the molecular ring. The results in this article support an initial decomposition step which leaves the ring intact, but subsequent ring cleavage is suggested to rapidly follow. The evidence supporting an intact molecular ring is the occurrence of the nitroxide spectrum in Fig. 1. The cyclic nitroxide (I) can be derived from the parent RDX molecule by a net loss of NO. There are at least two mechanisms for this: 1) homolytic cleavage of an $N-NO_2$ bond followed by reaction with molecular oxygen as shown in [1] or 2) recombination and rearrangement resulting in the loss of NO as in [2].

The conditions for detecting radical I are dependent on the RDX concentration in sulfolane and the time of heating. We found that a "low" concentration (0.1M) was required to observe I and that after heating the sample for approximately 30 minutes the spectrum slowly changed into the spectrum shown in Fig. 2. The 1M sample never gave a spectrum as in Fig. 1, but always appeared as in Fig. 2. This suggests that radical I is an intermediate radical which is converting into a second free radical (as indicated in [3]). We observed no gas evolution from the samples of RDX plus sulfolane at 170°C. When the temperature was increased gases were evolved but no nitric oxide was detected by using the "iron ring" test.[9] This suggests that the nitrogen dioxide and nitric oxide may be reacting with the solvent molecules. If so, then a solvent which is unreactive should depress the formation of radical I. A test with RDX (0.1M) in propylene carbonate at 170°C gave no EPR signals. This is weak but favorable evidence for equation [2]. Another possibility is that the nitroxide radicals (I) are reacting with each other to give a second radical. Disproportionation of nitroxides with alpha protons according to [4] is not uncommon (although neither product is predicted to be a free radical).

The radical structural assignment for the EPR spectrum in Fig. 2 and 3 is uncertain because of the complexity of the spectrum. The coupling assignment in Fig. 2b does offer a basis for suggesting a structure. The 9.98 G coupling may be assigned to 1 proton. The 8.21 G coupling is assigned to 1 nitrogen-14 coupling. The 6.66 G coupling is assigned to 4 equivalent protons. The 3.4 G coupling is assigned to 1 proton and the 1.25 G coupling is assigned to a different proton. A plausible structure (this is a tentative assignment) is indicated as II in Table I. It is also possible that a bi-radical is responsible for the spectrum in Fig. 2 and 3. Such a structure would resemble III in Table I. Attempts to deduce an unambiguous structure have been unsuccessful but further experiments using isotopic substitution are planned.

[1] 

[2] 

[3] 

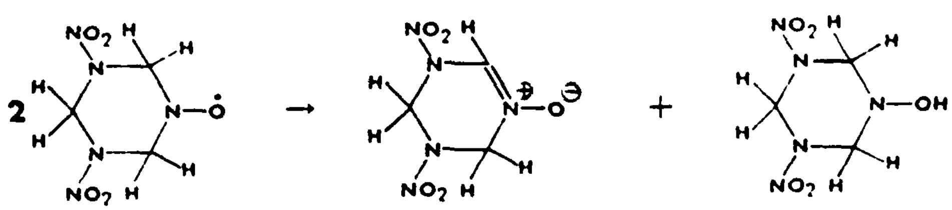
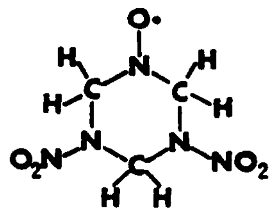
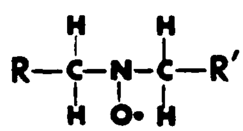
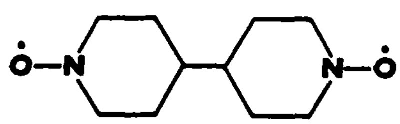
[4] 

Table 1

Free Radical and Molecular Structure Assignments Based Upon EPR Results

Designation	Structure
I.	
II. (tentative)	 Where R and R′ = aliphatic groups
III. (tentative)	

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